ROTATIONAL DYNAMICS OF THE MAGNETIC PARTICLES IN FERROFLUIDS *

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Abstract

A new theory for the dynamics of the magnetic particles and their magnetic moments in ferrofluids is developed. Based on a generalized Lagrangian formulation for the equations of motion of the colloidal particle, we introduce its interaction with the solvent fluid via dissipative and random noise torques, as well as the interactions between the particle and its magnetic moment, treated as an independent physical entity and characterized by three generalized coordinates, its two polar angles and its modulus. It has been recognized recently that inertial effects, as well as the particle's rotational Brownian motion, may play important roles on the dynamic susceptibility of a class of magnetic fluids. No satisfactory theory existed, up to now, that takes this effects into account. The theory presented here is a first-principles 3-dimensional approach, in contrast to some phenomenological 2-dimensional approaches that can be found in the recent literature. It is appropriate for superparamagnetic, non-superparamagnetic and mixed magnetic fluids. As a simple application, the blocked limit (magnetic moment fixed in the particle) is treated numerically. The rotational trajectory of the particles in presence of a magnetic field, as well as the response functions and dynamic susceptibility matrices are explicitly calculated for some values of the parameters

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I. INTRODUCTION

Considerable interest has been shown, in recent years, on the dynamics of the magnetization of ferrofluids in presence of applied magnetic fields and on the corresponding complex magnetic susceptibility. Just to give a few examples of recently published work on the field we mention the theoretical works by Raikher and Rusakov [1], Coffey and Kalmykov [2], Shliomis and Stepanov [3], the experimental works by Morais et al. [4], Fannin et al. [5], Vincent et al. [6] and an experimental-theoretical paper by Fannin et al. [7] . Certainly, this increased interest in a better understanding of the behavior of these materials is related to their renewed technological importance, with various new applications [8].

The usual theoretical approach to calculate the dynamic susceptibility is based on Gilbert's [9] or Landau Lifshitz' [10] equation (which are equivalent) for the dynamics of the magnetic moment, with the addition of noise, following the pioneering work of Brown [11]. Several authors use these equations of motion to calculate relaxation times and the susceptibility is then borrowed from Debye's theory [12].

Two distinct rotational relaxation mechanisms may coexist in ferrofluids: the Néel relaxation, by which the magnetic moment moves with respect to the mechanical particle, and the Brownian, or Debye relaxation, corresponding to the particle's rotation inside the fluid. In most experimental situations one of these mechanisms is dominant, and this may be the reason why there is not, up to now, that we know, a satisfactory theory, sufficiently general to be applied for all situations, from the pure Néel to the pure Brownian relaxation, passing by all possible combinations of those mechanisms. In this respect the model of "two spheres", by Fannin and Coffey [13] should be mentioned as a first effort.

The purpose of the present paper is to present such a general theory. The main limitation of our approach is that we deal only with axially symmetric particles, with easy axis of magnetization parallel to the symmetry axis. However, the magnetic moment is allowed to rotate inside the particle, as well as to have an oscillating modulus, and the particle is allowed to rotate with respect to the solvent, which is immobile with respect to the laboratory. The suspension is considered sufficiently dilute for the particle-particle interaction to be negligible, so that we deal only with single particle dynamics. However, in a mean field approximation, our approach can serve as a starting point for the inter-particle interactions to be considered in future works.

In section II we write the equations of the rotational motion of an axially symmetric particle inside a fluid (Langevin-type equations), based on the generalized Euler-Lagrange equations. In section III we obtain, from the equations of section II, in a convenient limit, the equations of motion for the magnetic moment $\boldsymbol{\mu}$, which reduce, in the case of constant modulus of $\boldsymbol{\mu}$, to the Gilbert's equation. In section IV we arrive at the set of six coupled equations, for the six degrees of freedom, the three Euler angles of the particle's rotations, the two polar angles of $\boldsymbol{\mu}$ and its modulus. Some less general situations are also considered in this section, as particular cases. In section V the "blocked limit", i.e., when the magnetic moment is fixed with respect to the particle, is treated as an explicit example of application. In section VI we introduce a simple version of linear response theory, applicable for the cases where the noise can be considered only for its effect as a thermal bath. In section VII we apply this linear response approach to calculate the dynamic susceptibility of the ferrofluid in the blocked limit and in section VIII some numerical results are presented and discussed.

We do not explore, in the present paper, the set of six equations of section IV, Eqs. (11), in its great generality, because this would make the paper too long. Work with this purpose is being carried out by the authors, to be published in future papers.

II. ROTATIONAL DYNAMICS OF A PARTICLE IN A FLUID

Consider a particle of axially symmetric shape in suspension in a fluid. The principal moments of inertia will be denoted by $I_1 = I_2$ and I_3. Disregarding translational degrees of freedom, its Lagrangian may be written in terms of the Euler angles θ, ϕ and ψ (in the notation of Goldstein [14]), taken as generalized coordinates, as

$$L = \frac{I_1}{2}(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta) + \frac{I_3}{2}(\dot{\psi} + \dot{\phi}\cos\theta)^2 - V(\theta, \phi) \tag{1}$$

where $V(\theta, \phi)$ is some orientation dependent potential. It cannot depend on ψ because of the axial symmetry of the particle.

The interaction forces (torques) between the particle and the fluid are of the dissipative and noise types. Therefore, they are not included in the Lagrangian, but instead, we have to use the "generalized Euler-Lagrange equations", with the corresponding torques, represented by Q_i, at the right hand side:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = Q_i \ , \tag{2}$$

where $q_i = \theta, \phi$ or ψ.

We write the non-conservative torques Q_i as sums of dissipative and noise terms, in the form

$$Q_i = -\frac{\partial \mathcal{F}}{\partial \dot{q}_i} + \Gamma_i(t) \ , \tag{3}$$

where $\mathcal{F}$ is the following Rayleigh dissipation function [14],

$$\mathcal{F} = \frac{1}{2}\lambda((\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta) + \frac{1}{2}\lambda'(\dot{\psi} + \dot{\phi}\cos\theta)^2, \tag{4}$$

and $\Gamma_i(t)$ are the noise torques. The dissipation constants λ and λ' may be different because λ' is associated with the particle rotation around the symmetry axis, while λ is associated with the rotations perpendicular to it. Substituting Eqs. (1), (3) and (4) into Eq. (2) we obtain the following system of equations for the particle's rotation:

$$I_1(\ddot{\theta} - \dot{\phi}^2 \sin\theta\cos\theta) + I_3\ \dot{\phi}\ (\dot{\psi} + \dot{\phi}\cos\theta)\sin\theta + \lambda\ \dot{\theta} + V_\theta = \Gamma_\theta \ , \tag{5a}$$

$$\begin{aligned} &I_1(\ddot{\phi}\sin^2\theta + 2\ \dot{\phi}\ \dot{\theta}\sin\theta\cos\theta) + I_3\cos\theta\ \frac{d}{dt}(\dot{\psi} + \dot{\phi}\cos\theta) + \\ &-I_3(\dot{\psi} + \dot{\phi}\cos\theta)\dot{\theta}\sin\theta + \lambda\ \dot{\phi}\sin^2\theta + V_\phi = \Gamma_\phi \ , \end{aligned} \tag{5b}$$

$$I_3\frac{d}{dt}(\dot{\psi} + \dot{\phi}\cos\theta) + \lambda'\ (\dot{\psi} + \dot{\phi}\cos\theta) = \Gamma_\psi. \tag{5c}$$

where $V_\theta = \partial V/\partial\theta$ and $V_\phi = \partial V/\partial\phi$. The expression $(\dot\psi + \dot\phi\cos\theta)$ was left unbroken wherever it appears in the above equations because it represents the component of the angular velocity vector $\boldsymbol{\omega}$ along the symmetry axis and we make use of this fact in the interpretation of the dissipative torques in terms of the components of $\boldsymbol{\omega}$, as follows.

Let us define the following four unit vectors: $\boldsymbol{z}$, along the laboratory z-axis, $\boldsymbol{c}$, along the particle's symmetry axis, $\boldsymbol{a}$, perpendicular to the plane containing $\boldsymbol{c}$ and $\boldsymbol{z}$ ($\widehat{\boldsymbol{cz}}$-plane) and $\boldsymbol{b}$, perpendicular to the $\widehat{\boldsymbol{ca}}$-plane, namely,

$$\boldsymbol{z} = (0,\ 0,\ 1)\ , \tag{6a}$$
$$\boldsymbol{c} = (\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)\ , \tag{6b}$$
$$\boldsymbol{a} = \frac{\boldsymbol{z}\times\boldsymbol{c}}{\sin\theta} = (-\sin\phi, \cos\phi, 0)\ , \tag{6c}$$
$$\boldsymbol{b} = \boldsymbol{c}\times\boldsymbol{a} = (-\cos\theta\cos\phi,\ -\cos\theta\sin\phi,\ \sin\theta)\ . \tag{6d}$$

As a notation to be used throughout this work, subscripts $z,\ c,\ a$ or b on a vector indicate its orthogonal projection on the $\boldsymbol{z}$, $\boldsymbol{c}$, $\boldsymbol{a}$ or $\boldsymbol{b}$ directions and subscript $\bar{c}$ indicates the vector's projection on the plane perpendicular to $\boldsymbol{c}$.

The particle's angular velocity vector $\boldsymbol{\omega}$ may be decomposed into a sum of two vectors, perpendicular and parallel to $\boldsymbol{c}$, respectively,

$$\boldsymbol{\omega} = \boldsymbol{\omega}_{\bar{c}} + \omega_c\ \boldsymbol{c}\ ,$$

with

$$\boldsymbol{\omega}_{\bar{c}} = \boldsymbol{c}\times\dot{\boldsymbol{c}} = (-\dot\theta\sin\phi - \dot\phi\sin\theta\cos\theta\cos\phi,\ \dot\theta\cos\phi - \dot\phi\sin\theta\cos\theta\sin\phi,\ \dot\phi\sin^2\theta)$$

and

$$\omega_c = \dot\psi + \dot\phi\cos\theta\ .$$

The orthogonal projection of $\boldsymbol{\omega}_{\bar{c}}$ on the z-axis is

$$\omega_{\bar{c}z} = \boldsymbol{\omega}_{\bar{c}}\cdot\boldsymbol{z} = \dot\phi\sin^2\theta\ ,$$

and the orthogonal projection of $\boldsymbol{\omega}$ (or of $\boldsymbol{\omega}_{\bar{c}}$) on the direction perpendicular to the $\widehat{\boldsymbol{cz}}$ plane is

$$\omega_a = \boldsymbol{\omega}\cdot\boldsymbol{a} = \boldsymbol{\omega}_{\bar{c}}\cdot\boldsymbol{a} = \dot\theta\ .$$

Thus we see that the dissipative torques present in Eqs. (5a), (5b) and (5c) are given by ω_a, $\omega_{\bar{c}z}$ and ω_c, respectively, times the dissipation parameters λ or λ'.

The noise torques will be treated along these same lines. We start by defining the noise torque vector by its orthogonal components,

$$\boldsymbol{\Gamma} = \Gamma_a\ \boldsymbol{a} + \Gamma_b\ \boldsymbol{b} + \Gamma_c\ \boldsymbol{c}\ .$$

The noise becomes completely defined by stating the statistics of its three components. The usual procedure is to consider them as statistically independent, Gaussian white noise.

This is, however, not a necessary assumption and we leave it open for future modeling. What we need now is to know how the three components come into Eqs. (5). Guided by the above decomposition of the dissipative torque, we are led to identify

$$
\begin{aligned}
\Gamma_\theta &= \Gamma_a \; , \\
\Gamma_\phi &= \Gamma_{\bar{c}z} = \boldsymbol{\Gamma}_{\bar{c}} \cdot \boldsymbol{z} = \Gamma_b \; \sin\theta \; , \\
\Gamma_\psi &= \Gamma_c \; .
\end{aligned}
$$

Before we proceed to deduce the equations of motion for the general case of magnetic particles in ferrofluids we show, in the next section, how to obtain, from Eqs. (5), the equations of motion for the spherical coordinates of a mono-domain magnetic moment.

III. EQUATIONS OF MOTION FOR A MAGNETIC MOMENT

The magnetic moment $\boldsymbol{\mu}$ of a mono-domain particle is related to its internal angular momentum $\boldsymbol{S}$ by $\boldsymbol{\mu} = \gamma \boldsymbol{S}$, where γ is the gyromagnetic factor. Although the modulus S of $\boldsymbol{S}$ is taken as constant in most works on superparamagnetism and magnetic fluids, for very small particles its oscillation may be significant and we prefer to allow it to be time dependent. The modern technology allows the preparation of samples with magnetic particles whose diameters are smaller than $20\mathring{A}$ [15] and superparamagnetic clusters containing only 12 magnetic atoms have also been reported [16]. We can model the magnetic moment by a rotating charged particle, in the limit of zero moments of inertia, $I_1 \to 0$, $I_3 \to 0$, and $\dot{\psi} \to \infty$ so that $I_3 \dot{\psi} = S$. Because in the next section we will work with the joint system, a particle and its fluctuating magnetic moment, we write the generalized coordinates, potential energy, dissipative and noise torques, with a notation distinct from that corresponding to the particle. Namely, we make the following substitutions: $\theta \to \vartheta$, $\phi \to \varphi$, $I_3\,\dot{\psi} \to S$, $V \to W$, $\lambda \to \xi$, $\lambda' \to \xi'$ and $\Gamma \to \mathcal{T}$. We also introduce two modifications in the equation corresponding to Eq. (5c), namely, we write $S - S_0$ instead of S in the dissipative term and introduce a torque W_s, whose origin will be explained below. In the said limit and with the new notation the system of Eqs. (5) becomes:

$$
S\,\dot{\varphi}\sin\vartheta + \xi\,\dot{\vartheta} + W_\vartheta = \mathcal{T}_\vartheta \; , \tag{7a}
$$

$$
\dot{S}\cos\vartheta - S\,\dot{\vartheta}\sin\vartheta + \xi\,\dot{\varphi}\sin^2\vartheta + W_\varphi = \mathcal{T}_\varphi \; , \tag{7b}
$$

$$
\dot{S} + \xi'(S - S_0) + W_s = \mathcal{T}_s. \tag{7c}
$$

Here we have written $S - S_0$, instead of S, in the dissipation term of Eq. (7c) to account for the fact that the relaxation of the fluctuations of S is towards a most probable (equilibrium) value S_0 and not towards 0. It may appear strange that, even though we have derived the equations of motion for $\boldsymbol{S}$ from the equations of motion for a symmetric particle, in a convenient limit, we have now to add a term "ad hoc" (S_0), which does not have an equivalent in the particle's equations. This is so because in classical physics the equilibrium magnetization is always zero. Non-zero equilibrium magnetic moments can only exist because of the quantum mechanical nature of matter and, therefore, cannot be deduced from a pure

classical approach. The torque W_s was introduced because a crystal field may have an effective interaction with $\boldsymbol{\mu}$, with origin in an orbital contribution to $\boldsymbol{S}$ [24], with a possible torque component parallel to $\boldsymbol{S}$. There is not an equivalent term in Eq. (5c) because of the assumed axial symmetry of the particle.

It is interesting to study the behavior of Eqs. (7) in the absence of noise, $\mathcal{T}_i = 0$ and with $W_s = 0$. Eq. (7c) has then the trivial stationary solution $S = S_0$. Assuming this constant value for S in Eqs. (7a) and (7b) they reduce to

$$S_0\, \dot\varphi \sin\vartheta + \xi\, \dot\vartheta + W_\vartheta = 0\ , \tag{8a}$$

$$-S_0\, \dot\vartheta \sin\vartheta + \xi\, \dot\varphi \sin^2\vartheta + W_\varphi = 0\ . \tag{8b}$$

The conservative torques, $-W_\vartheta$ and $-W_\varphi$, have, usually, contributions from two different origins, the interaction of $\boldsymbol{S}$ with a crystalline, anisotropy field and/or with a magnetic field, which can also be of several different origins. In the case of magnetic field, $\boldsymbol{H}$, the potential energy is $W = -\boldsymbol{\mu}\cdot\boldsymbol{H}$. With a little of algebraic work one can show, in this case, that the set of Eqs. (8) is equivalent to the well known Gilbert's equation [9],

$$\frac{d\boldsymbol{\mu}}{dt} = \gamma\ \boldsymbol{\mu} \times \left[\boldsymbol{H} - \frac{\xi}{\mu^2}\frac{d\boldsymbol{\mu}}{dt}\right]\ ,$$

for $\boldsymbol{\mu} = \gamma \boldsymbol{S}$ and $S = S_0$. This equation was used by W. F. Brown [11] as a starting point for his stochastic theory of superparamagnetism, where he assumed the magnetic field $\boldsymbol{H}$ to contain a noise term. A more general theory for superparamagnetism, which allows also for oscillations on the modulus $\mu = \gamma S$ of the magnetic moment, was worked out by Ricci and Scherer [17–19], based on the set of Eqs. (7). For this reason we will not continue to explore the consequences of Eqs. (7) in the present paper, turning, instead, to the more general ferrofluid, where the rotations of the mechanical particle are taken into account, in addition to the motion of $\boldsymbol{S}$ relative to the particle.

IV. THE GENERAL FERROFLUID

In recent years several researchers [1,4,13,20] have drawn attention to the importance of the motion of the magnetic particle, its inertia and viscous interaction with the fluid, to the dynamic magnetic susceptibility of ferrofluids. A theoretical treatment of this problem, which is both, more fundamental and more general than those previously published, follows naturally from the context described above.

Taken together, the systems of Eqs. (5) and (7) contain all the degrees of freedom relevant to the problem. To the potential energy terms, V in Eqs. (5) and W in Eqs. (7), the interaction energy between the magnetic moment and the particle, which we will denote by U, has to be added. Due to the particle's symmetry, this term can only depend on S and on the angle between $\boldsymbol{S}$ and the symmetry axis, $\boldsymbol{c}$. It is convenient to define another orthogonal set of unit vectors, related to the direction of the magnetic moment, namely, $\boldsymbol{s}$, in the $\boldsymbol{S}$ direction, $\boldsymbol{u}$, perpendicular to the $\widehat{\boldsymbol{sz}}$-plane and $\boldsymbol{v}$, perpendicular to the $\widehat{\boldsymbol{su}}$-plane,

$$\boldsymbol{s} = \frac{\boldsymbol{S}}{S} = (\sin\vartheta\cos\varphi,\ \sin\vartheta\sin\varphi,\ \cos\vartheta)\ , \tag{9a}$$

$$\boldsymbol{u} = \frac{\boldsymbol{z}\times\boldsymbol{s}}{\sin\vartheta} = (-\sin\varphi, \cos\varphi, 0)\ , \tag{9b}$$

$$\boldsymbol{v} = \boldsymbol{s}\times\boldsymbol{u} = (-\cos\vartheta\cos\varphi,\ -\cos\vartheta\sin\varphi,\ \sin\vartheta)\ . \tag{9c}$$

The interaction energy U can then be written as $U(S, \boldsymbol{s}\cdot\boldsymbol{c})$. In principle the particle can interact also with other fields, besides $\boldsymbol{H}$, as is the case if it has an electric dipole and an electric field is present. For this reason we keep also the potential energy $V(\theta, \phi)$ in the new set of equations.

The dissipative interaction associated with the rotation of $\boldsymbol{S}$ relative to the particle will be written in terms of the relative angular velocity vector. Since only rotations perpendicular to $\boldsymbol{S}$ can lead to a meaningful interaction torque with origin on the relative motion, we define the relative angular velocity $\boldsymbol{\omega}_r$ as

$$\boldsymbol{\omega}_r = \boldsymbol{\varpi} - \boldsymbol{\omega}_{\bar{s}}\ ,$$

where

$$\boldsymbol{\varpi} = \boldsymbol{s}\times\dot{\boldsymbol{s}}$$

is the angular velocity of rotation of the magnetic moment with respect to the laboratory and

$$\boldsymbol{\omega}_{\bar{s}} = \boldsymbol{s}\times\boldsymbol{\omega}\times\boldsymbol{s} = \boldsymbol{\omega} - (\boldsymbol{s}\cdot\boldsymbol{\omega})\boldsymbol{s}\ .$$

is the orthogonal projection of the particle's angular velocity $\boldsymbol{\omega}$ on the plane perpendicular to $\boldsymbol{S}$. The dissipative interaction torque on the particle is then $+\xi\ \boldsymbol{\omega}_r$. The plus sign is because of the way we defined $\boldsymbol{\omega}_r$, where the particle's angular velocity appears with a minus sign. Guided by the interpretation of the dissipative torque terms of Eqs. (5) in terms of angular velocity components, as explained bellow the said equations, we write down immediately the dissipative torque terms to be added to the left-hand sides (therefore, with a $-$ sign) of Eqs. (5), namely

$$\begin{aligned}
&-\xi\,\omega_{ra} = -\xi\,\boldsymbol{\omega}_r\cdot\boldsymbol{a}\ ,\\
&-\xi\,\omega_{r\bar{c}z} = -\xi\,[\boldsymbol{\omega_r} - (\boldsymbol{\omega_r}\cdot\boldsymbol{c})\,\boldsymbol{c}]\cdot\boldsymbol{z} = -\xi\,(\omega_{rz} - \omega_{rc}\cos\theta\ ,\\
&-\xi\,\omega_{rc} = -\xi\ \boldsymbol{\omega}_r\cdot\boldsymbol{c}\ .
\end{aligned}$$

Of course, all this scalar products, as well as those which follow, in the next equations, may be easily written as functions of the four angles θ, ϕ, ϑ and φ and their time derivatives, by using Eqs. (6) and (9). However, because scalar products are very easily handled in numerical procedures, we prefer to leave them in this form.

Clearly, the torque on the magnetic moment, due to the relative motion, is the "reaction" to the torque on the particle, i.e., it is equal to $-\xi\boldsymbol{\omega}_r$, and, in place of $\xi\ \dot{\vartheta}$ and $\xi\ \dot{\varphi}\sin^2\vartheta$ in Eqs. (7) we shall use (remembering that $\boldsymbol{\omega}_{r\bar{s}} = \boldsymbol{\omega}_r$)

$$\begin{aligned}
\xi\,\omega_{ru} &= \xi\,\boldsymbol{\omega}_r\cdot\boldsymbol{u}\ ,\\
\xi\,\omega_{rz} &= \xi\,\boldsymbol{\omega}_r\cdot\boldsymbol{z}\ .
\end{aligned}$$

No term coming from the relative angular velocity $\boldsymbol{\omega}_r$ has to be added to Eq. (7c) because $\boldsymbol{\omega}_r$ is perpendicular to $\boldsymbol{S}$. However, there is the term $\xi'\,(S-S_0)$ already present in that equation, with origin in the (quantum) fluctuations of S, and this term will be kept. Since angular momentum has to be conserved, its reaction counterpart on the particle has to be added to Eqs. (5). Calling

$$\boldsymbol{\mathcal{R}} = (S-S_0)\;\boldsymbol{s}\;,$$

the terms to be added to the left-hand sides of Eqs. (5) are

$$\begin{aligned}
&-\xi'\,\mathcal{R}_a = -\xi'\,\boldsymbol{\mathcal{R}}\cdot\boldsymbol{a} = -\xi'\,(S-S_0)\,\boldsymbol{s}\cdot\boldsymbol{a}\;,\\
&-\xi'\,\mathcal{R}_{\bar{c}z} = -\xi'\,[\boldsymbol{\mathcal{R}}-(\boldsymbol{\mathcal{R}}\cdot\boldsymbol{c})\,\boldsymbol{c}]\cdot\boldsymbol{z} = -\xi'\,(S-S_0)[\boldsymbol{s}-(\boldsymbol{s}\cdot\boldsymbol{c})\,\boldsymbol{c}]\cdot\boldsymbol{z}\;,\\
&-\xi'\,\mathcal{R}_c = -\xi'\,\boldsymbol{\mathcal{R}}\cdot\boldsymbol{c} = -\xi'\,(S-S_0)\,\boldsymbol{s}\cdot\boldsymbol{c}\;.
\end{aligned}$$

The noise torques of interaction between the particle and the magnetic moment can be written down along the same lines of procedure as done for the noise torques of the fluid on the particle, at the end of section II. We assume three orthogonal, independent, noise torque vectors, along the unit vectors defined with respect to the direction of the magnetic moment:

$$\boldsymbol{\mathcal{T}} = \mathcal{T}_s\;\boldsymbol{s} + \mathcal{T}_u\;\boldsymbol{u} + \mathcal{T}_v\;\boldsymbol{v}\;. \tag{10}$$

Being $\boldsymbol{\mathcal{T}}$ the torque on the magnetic moment, then the torque on the particle is $-\boldsymbol{\mathcal{T}}$. Following the same line of reasoning as done before, we identify the torques in Eqs. (7):

$$\begin{aligned}
&\mathcal{T}_\vartheta = \mathcal{T}_u\;,\\
&\mathcal{T}_\varphi = \mathcal{T}_{\bar{s}z} = \mathcal{T}_v\sin\vartheta\;,\\
&\mathcal{T}_s = \mathcal{T}_s\;.
\end{aligned}$$

Correspondingly, we the following terms have to be added to the right-hand-sides of Eqs. (5):

$$\begin{aligned}
&\mathcal{T}_\theta = -\mathcal{T}_a = -\boldsymbol{\mathcal{T}}\cdot\boldsymbol{a}\;,\\
&\mathcal{T}_\phi = -\mathcal{T}_{\bar{c}z} = -[\boldsymbol{\mathcal{T}}-(\boldsymbol{\mathcal{T}}\cdot\boldsymbol{c})\,\boldsymbol{c}]\cdot\boldsymbol{z}\;,\\
&\mathcal{T}_\psi = -\mathcal{T}_c = -\boldsymbol{\mathcal{T}}\cdot\boldsymbol{c}\;.
\end{aligned}$$

Therefore, the state of the composed system, the particle and its magnetic moment, is described by the 6 generalized coordinates, θ, ϕ, ψ, ϑ, φ and S, whose dynamical behavior is governed by the following set of coupled differential equations:

$$I_1(\ddot\theta - \dot\phi^2 \sin\theta\cos\theta) + I_3\ \dot\phi\ (\dot\psi + \dot\phi\cos\theta)\sin\theta + \lambda\ \dot\theta - \xi\omega_{ra} +$$
$$-\xi'\ \mathcal{R}_a + V_\theta + U_\theta = \Gamma_a - \mathcal{T}_a\ , \tag{11a}$$

$$I_1(\ddot\phi\sin^2\theta + 2\ \dot\phi\ \dot\theta\sin\theta\cos\theta) + I_3\cos\theta\ \frac{d}{dt}(\dot\psi + \dot\phi\cos\theta) +$$
$$-I_3(\dot\psi + \dot\phi\cos\theta)\dot\theta\sin\theta + \lambda\ \dot\phi\sin^2\theta - \xi\omega_{r\bar{c}z} - \xi'\ \mathcal{R}_{\bar{c}z} + V_\phi + U_\phi = \Gamma_b\sin\theta - \mathcal{T}_{\bar{c}z}\ , \tag{11b}$$

$$I_3\frac{d}{dt}(\dot\psi + \dot\phi\cos\theta) + \lambda'\ (\dot\psi + \dot\phi\cos\theta) - \xi\omega_{rc} - \xi'\ \mathcal{R}_c = \Gamma_c - \mathcal{T}_c\ , \tag{11c}$$

$$S\ \dot\varphi\sin\vartheta + \xi\omega_{ru} + W_\vartheta + U_\vartheta = +\mathcal{T}_u\ , \tag{11d}$$

$$\dot S\cos\vartheta - S\ \dot\vartheta\sin\vartheta + \xi\omega_{r\bar{c}z} + W_\varphi + U_\varphi = +\mathcal{T}_{\bar{s}z}\ , \tag{11e}$$

$$\dot S + \xi'(S - S_0) + U_S = \mathcal{T}_s\ . \tag{11f}$$

This set of six equations is of very general applicability on ferrofluids. It allows for a large variety of modeling: There are three independent conservative interaction potentials, V, U and W, four dissipative parameters, λ, λ', ξ, and ξ', and also the noise torques $\mathbf{\Gamma}$ and $\boldsymbol{\mathcal{T}}$, whose statistical properties are open for modeling. Particle-particle interaction was not explicitly taken into account, but on a mean-field approximation it can be included in V and/or in W.

As we mentioned before, in most cases of practical interest the fluctuations in the modulus S can be neglected. In this case Eqs. (11) become simpler, in several respects: Eq. (11f) ceases to exist, all terms in $\dot S$ and in ξ' become zero and the noise term $\mathcal{T}_s$ in Eq. (10) and its contribution in Eqs. (11) also vanish.

Two interesting limit situations are readily obtained from Eqs(11), the "superparamagnetic" limit, for which the particle's coordinates, θ, ϕ, and ψ, are taken as constants, so that the system reduces to the last three equations, and the "blocked" limit (also called "Brownian" limit [21] or "inertial limit" [2]), when the magnetic moment is blocked along the particle's symmetry direction, i.e., $\vartheta = \theta$ and $\varphi = \phi$, but the particle can rotate inside the fluid. The superparamagnetic limit has been treated in three previous papers by Ricci and Scherer [17–19] and also by other authors. In the remaining sections of this paper we will deal with the "blocked" limit.

V. DYNAMICS OF THE MAGNETIC MOMENT IN THE BLOCKED LIMIT

We consider now the situation in which the magnetic moment is blocked along the particle's symmetry axis. This may happen because the sample is kept below the "blocking temperature" T_B [22] or because the material is so highly anisotropic that the magnetic moments only exists parallel to the easy axis [16]. The particle is still immersed in a fluid carrier, being able to rotate, together with its magnetic moment.

In terms of the set of Eqs. (11), the blocked limit is obtained by assuming an interaction potential U of the form $-U_0\delta(\boldsymbol{s}-\boldsymbol{c})$, with $U_0 \to \infty$, so that the only states energetically possible are those with $\boldsymbol{s}=\boldsymbol{c}$, i.e., $\vartheta=\theta$ and $\varphi=\phi$. By summing Eq. (11a) with Eq. (11d) and Eq. (11b) with Eq. (11e) the interaction terms U_θ and U_ϑ as well as U_ϕ and U_φ cancel out. The terms containing ω_{ra}, $\omega_{r\bar{c}z}$, $\mathcal{R}_a$, $\mathcal{R}_{\bar{c}z}$, $\boldsymbol{\mathcal{T}}_a$, and $\boldsymbol{\mathcal{T}}_{\bar{c}z}$ become identically zero, and $\mathcal{R}_c$ becomes $(S-S_0)$. Choosing θ and ϕ to denote the common polar angles, the system of equations becomes:

$$
\begin{aligned}
&I_1(\ddot{\theta}-\dot{\phi}^2\sin\theta\cos\theta)+I_3\,\dot{\phi}\,(\dot{\psi}+\dot{\phi}\cos\theta)\sin\theta+\lambda\,\dot{\theta}+V_\theta+\\
&+S\,\dot{\phi}\sin\theta+W_\theta=\Gamma_a\ ,
\end{aligned}
\tag{12a}
$$

$$
\begin{aligned}
&I_1(\ddot{\phi}\sin^2\theta+2\,\dot{\phi}\,\dot{\theta}\sin\theta\cos\theta)+I_3\cos\theta\,\frac{d}{dt}(\dot{\psi}+\dot{\phi}\cos\theta)+\\
&-I_3(\dot{\psi}+\dot{\phi}\cos\theta)\dot{\theta}\sin\theta+\lambda\,\dot{\phi}\sin^2\theta+V_\phi+\dot{S}\cos\theta\ +\\
&-S\,\dot{\theta}\sin\theta+W_\phi=\Gamma_b\sin\theta\ ,
\end{aligned}
\tag{12b}
$$

$$
I_3\frac{d}{dt}(\dot{\psi}+\dot{\phi}\cos\theta)+\lambda'\,(\dot{\psi}+\dot{\phi}\cos\theta)-\xi'(S-S_0)=\Gamma_c-\mathcal{T}_c\ ,
\tag{12c}
$$

$$
\dot{S}+\xi'(S-S_0)=+\mathcal{T}_c\ .
\tag{12d}
$$

We will not explore, in the present paper, the system of Eqs. (12) in all its generality. In the following we will consider only the cases when the noise terms do not need to be taken into account explicitly. The explicit presence of white noise torques makes of Eqs. (11) and (12) Ito-Langevin systems and their treatment demands the use of stochastic calculus. This will be treated in a future paper. Several circumstances may be devised where neglecting the noise is a good approximation. One of them is when the system is drawn far from equilibrium, in presence of a strong magnetic field, with $\mu H \gg k_B T$. Then the relaxation to the new equilibrium state, with $\boldsymbol{\mu}$ approximately parallel to $\boldsymbol{H}$, proceeds without an important influence of the noise. The Bloch's equations of magnetic resonance are based on this idea: they contain relaxation terms (with relaxation times T_1 and T_2), but no noise terms. Another interesting circumstance is in the context of linear response theory. The usual formulation considers the noise sufficiently weak for its effect to be only in establishing an initial thermal equilibrium. The perturbing field is then introduced adiabatically, i.e., with the system disconnected from the thermal bath. A similar approach to linear response, however based on the equations of motion, instead of based on the Liouville equation for the probability distribution, which is the case of Kubo's linear response theory [23], will be presented in the next section.

In the following we will also assume a constant modulus for the magnetic moment, i.e., $S=S_0$, and for the interaction potential we consider only $W=-\boldsymbol{\mu}\cdot\boldsymbol{H}=-\gamma S_0\boldsymbol{s}\cdot\boldsymbol{H}$. For simplicity, only a constant field, $\boldsymbol{H}=H_0\boldsymbol{z}$, will be considered now, but in the section on linear response we will introduce also a time dependent transversal field.

With this simplifications, the system of Eqs. (12) becomes

$$
\begin{aligned}
&I_1(\ddot{\theta} - \dot{\phi}^2 \sin\theta\cos\theta) + I_3\, \dot{\phi}\, (\dot{\psi} + \dot{\phi}\cos\theta)\sin\theta + \lambda\, \dot{\theta} + \\
&+S_0\, \dot{\phi}\sin\theta + \gamma S_0 H_0 \sin\theta = 0\ , \qquad (13a)
\end{aligned}
$$

$$
\begin{aligned}
&I_1(\ddot{\phi}\sin^2\theta + 2\, \dot{\phi}\, \dot{\theta}\sin\theta\cos\theta) + I_3\cos\theta\, \frac{d}{dt}(\dot{\psi} + \dot{\phi}\cos\theta) + \\
&-I_3(\dot{\psi} + \dot{\phi}\cos\theta)\dot{\theta}\sin\theta + \lambda\, \dot{\phi}\sin^2\theta - S_0\, \dot{\theta}\sin\theta = 0 \qquad (13b)
\end{aligned}
$$

$$
I_3\frac{d}{dt}(\dot{\psi} + \dot{\phi}\cos\theta) + \lambda'\, (\dot{\psi} + \dot{\phi}\cos\theta) = 0\ . \qquad (13c)
$$

Eq. (13c) shows that, under the circumstances considered, and for any value that the function $\dot{\psi} + \dot{\phi}\cos\theta$ may have, due to initial conditions, it will relax exponentially to zero. Since we will consider, in what follows, only stationary initial conditions, its value will be taken as identically zero. This simplifies the above set of equations to

$$
I_1(\ddot{\theta} - \dot{\phi}^2 \sin\theta\cos\theta) + S_0\, \dot{\phi}\sin\theta + \lambda\, \dot{\theta} = -\gamma S_0 H_0 \sin\theta\ , \qquad (14a)
$$

$$
I_1(\ddot{\phi}\sin^2\theta + 2\, \dot{\phi}\, \dot{\theta}\sin\theta\cos\theta) - S_0\, \dot{\theta}\sin\theta + \lambda\, \dot{\phi}\sin^2\theta = 0\ . \qquad (14b)
$$

This equations may be solved numerically, for arbitrarily given parameters, I_1, S_0, λ and γH_0 and arbitrary initial conditions, by using standard methods. An example of solution is shown in Fig.1, in form of a rotational trajectory of the magnetic moment, drawn over a sphere to help visualization. The origin of the magnetic moment vector is at the center of the sphere and its head follows the trajectory on the surface. the magnetic field $\boldsymbol{H_0}$ is parallel to the line from the south to the north pole. For Fig.1-a the initial velocities $v_0 = \dot{\theta}(t_0)$ and $w_0 = \dot{\phi}(t_0)$ were arbitrarily chosen, for Figs.1-b and 1-c the initial velocities were calculated from Eqs. (37) and (38) of Sec.VIII. The dissipation parameter λ for Fig.1-c is 100 times the value used for Figs.1-a and 1-b. All other parameters and also the total time interval are the same for the three figures.

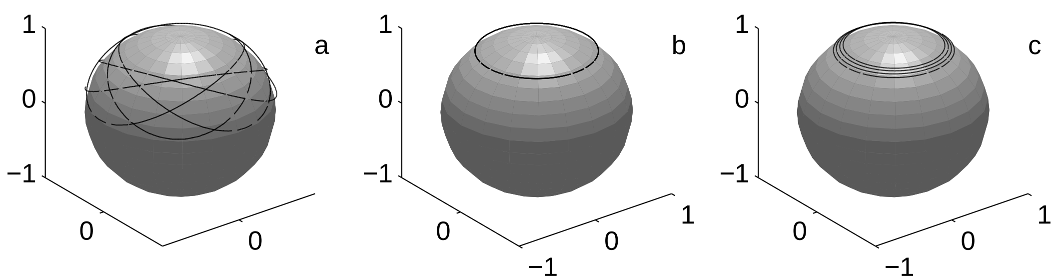

Fig.1: Trajectory of the head of the magnetic moment vector in its rotation around the constant magnetic field (see text). 1-a: for arbitrarily chosen initial velocities; 1-b: for initial velocities given according to Sec. VIII; 1-c: same as 1-b, but with dissipation parameter, λ, 100 times larger.

VI. A SIMPLE APPROACH TO LINEAR RESPONSE THEORY

The standard Linear Response Theory [23] is based on the classical or quantum Liouville Equation, for the probability distribution function or the density matrix, respectively, for systems in absence of noise, or based on the Fokker-Planck Equation in the case of stochastic processes [19]. A simpler approach, which has some limitations, but is appropriate for the purposes of this work, based on the equations of motion of the system, is as follows.

A. The Linear Equations for the Perturbation

Let us assume that the system's coordinates satisfy the equation

$$\dot{\boldsymbol{Q}}(t) = \boldsymbol{P}(\boldsymbol{Q}, t) \ , \tag{15}$$

where $\boldsymbol{Q} = (q_1, q_2, \cdots, q_n)$ and where $\boldsymbol{P} = (P_1, P_2, \cdots, P_n)$ are functions of the coordinates and of the time. We assume further that the only explicit time dependence of $\boldsymbol{P}$ comes from an applied perturbing field,

$$\boldsymbol{F}(t) = (F_1(t), \cdots, F_m(t)) \ ,$$

in the form

$$\boldsymbol{P}(\boldsymbol{Q}, t) = \boldsymbol{P}^0(\boldsymbol{Q}) + \widetilde{A}(\boldsymbol{Q}) \cdot \boldsymbol{F}(t) \ , \tag{16}$$

where $\widetilde{A}$ is an $n \times m$ matrix. The perturbation $\boldsymbol{F}(t)$ is assumed sufficiently weak for its effect in deviating $\boldsymbol{Q}(t)$ from its unperturbed values to be well approximated by a a linear functional. This approach is exact in the limit $\boldsymbol{F} \to 0$, which defines the initial susceptibility. In this equation and in what follows an upper index ^{0} (like in $\boldsymbol{P}^0$) will indicate "unperturbed values", while a lower index $_0$ (like in $\boldsymbol{Q}_0$) will be used for initial values. Therefore $\boldsymbol{Q}^0(t)$ indicates the solution of the unperturbed equation, with given initial conditions,

$$\dot{\boldsymbol{Q}}^0(t) = \boldsymbol{P}^0(\boldsymbol{Q}^0) \ , \qquad \boldsymbol{Q}^0(t_0) = \boldsymbol{Q}_0^0 = (q_{01}, \cdots, q_{0n}) \ . \tag{17}$$

The solution of Eq. (15) will be written as

$$\boldsymbol{Q}(t) = \boldsymbol{Q}^0(t) + \boldsymbol{X}(t) \ , \tag{18}$$

where $\boldsymbol{X}(t)$ is a linear functional of $\boldsymbol{F}$. Substituting Eq. (18) into Eq. (15), using Eq. (16) and keeping only linear terms in $\boldsymbol{F}$ follows

$$\dot{\boldsymbol{X}}(t) = \widetilde{K}(\boldsymbol{Q}^0(t)) \cdot \boldsymbol{X}(t) + \widetilde{A}(\boldsymbol{Q}^0(t)) \cdot \boldsymbol{F}(t) \ , \tag{19}$$

where the matrix elements of $\widetilde{K}$ are

$$K_{ij} = \frac{\partial P_i^0}{\partial q_j^0} \ . \tag{20}$$

Eq. (19) is a linear, inhomogeneous, system of equations for $\boldsymbol{X}$, with time dependent coefficients $K_{ij}(t) = K_{ij}(\boldsymbol{Q}^0(t))$. The corresponding homogeneous equation,

$$\dot{\boldsymbol{Y}} = \widetilde{K} \cdot \boldsymbol{Y} \tag{21}$$

has the solution

$$\boldsymbol{Y}(t) = \widetilde{M}(t, t_0) \cdot \boldsymbol{Y}_0 \ ,$$

where the matrix $\widetilde{M}$ is formally given by

$$\widetilde{M}(t, t_0) = \exp(\int_{t_0}^{t} \widetilde{K}(t')\, dt') \ . \tag{22}$$

The general solution of Eq. (19) may be written formally as

$$\boldsymbol{X}(t) = \widetilde{M}(t, t_0) \cdot \boldsymbol{X}_0 + \int_{t_0}^{t} \widetilde{M}(t, t') \cdot \widetilde{A}(t') \cdot \boldsymbol{F}(t')\, dt' \ .$$

Since $\boldsymbol{X}(t)$ has to be a linear functional of $\boldsymbol{F}$, it follows that $\boldsymbol{X}_0 = 0$. Thus

$$\boldsymbol{X}(t) = \int_{t_0}^{t} \widetilde{M}(t, t') \cdot \widetilde{A}(t') \cdot \boldsymbol{F}(t')\, dt' \ . \tag{23}$$

In numerical procedures, it is often simpler to solve Eq. (21) then to work with Eq. (22) to obtain the matrix elements of $\widetilde{M}$. To obtain $M_{ij}(t, t_0)$ from the solutions of Eq. (21) we define the set of n unit vectors of dimensionality n,

$$\begin{aligned} \boldsymbol{Y}_0^1 &= (1, 0, \cdots, 0) \\ \boldsymbol{Y}_0^2 &= (0, 1, \cdots, 0) \\ &\cdots\cdots\cdots\cdots\cdots \\ \boldsymbol{Y}_0^n &= (0, 0, \cdots, 1) \end{aligned}$$

The solution of Eq. (21), with initial condition $\boldsymbol{Y}(t_0) = \boldsymbol{Y}_0^i$ will be denoted by $\boldsymbol{Y}^i(t)$, i.e.,

$$\boldsymbol{Y}^i(t) = \widetilde{M}(t, t_0) \cdot \boldsymbol{Y}_0^i \ .$$

Therefore, the j^{th} component of $\boldsymbol{Y}^i(t)$ is

$$Y_j^i(t) = M_{ji}(t, t_0) \ , \tag{24}$$

from what follows that to obtain the matrix elements $M_{ji}(t, t_0)$ one solves the linear set of Eqs. (21) with the $\boldsymbol{Y}_0^i$ as initial vectors.

B. Response Function and Susceptibility Matrices

Consider the dynamical variable (observable) $\boldsymbol{B}(\boldsymbol{Q}) = (B_1, \cdots, B_m)$. Its ensemble average over the initial equilibrium distribution will be denoted by $\langle \boldsymbol{B}(\boldsymbol{Q}) \rangle_0$. The "response" of $\boldsymbol{B}$ to the perturbing field $\boldsymbol{F}(t)$ is defined by

$$\delta \boldsymbol{B}(t) \equiv \langle \boldsymbol{B}(\boldsymbol{Q}(t)) \rangle_0 - \left\langle \boldsymbol{B}(\boldsymbol{Q}^0(t)) \right\rangle_0 .$$

Expanding the first term above around $\boldsymbol{Q}^0$ to first order in $\boldsymbol{X}$ and using Eq. (23) follows

$$\delta \boldsymbol{B}(t) = \left\langle \widetilde{\nabla B}(t) \cdot \int_{t_0}^{t} \widetilde{M}(t,t') \cdot \widetilde{A}(t') \cdot \boldsymbol{F}(t')\, dt' \right\rangle_0 , \tag{25}$$

where $\widetilde{\nabla B}$ is an $m \times n$ matrix, with elements

$$(\nabla B)_{ki} \equiv B_{k,i} \equiv \left(\frac{\partial B_k}{\partial q_i} \right)_{Q=Q^0(t)} , \quad k = 1 \cdots m \, , \quad i = 1 \cdots n \, . \tag{26}$$

The "response function matrix" $(m \times m)$ $\widetilde{\Phi}$ is defined by

$$\delta \boldsymbol{B}(t) = \int_{t_0}^{t} \widetilde{\Phi}(t - t') \cdot \boldsymbol{F}(t')\, dt' \, . \tag{27}$$

Therefore, comparing Eqs. (27) and (25), we identify

$$\widetilde{\Phi}(t - t') = \left\langle \widetilde{\nabla B}(t) \cdot \widetilde{M}(t,t') \cdot \widetilde{A}(t') \right\rangle_0 , \tag{28}$$

which is function of $t - t'$ and not of t and t', independently, because the average is over the equilibrium distribution, for which absolute times are meaningless. Therefore, we can choose $t' = t_0 = 0$ in Eq. (28) and write the matrix elements of $\widetilde{\Phi}(t)$ as

$$\Phi_{kl}(t) = \sum_{ij} \langle B_{k,i}(t) M_{ij}(t,0) A_{jl}(0) \rangle_0 \, . \tag{29}$$

The complex susceptibility is defined as the Fourier-Laplace transform of $\widetilde{\Phi}$,

$$\chi_{kl}(\omega) = \lim_{\epsilon \to 0^+} \int_0^\infty \mathrm{exp(i\omega t' - \epsilon t')\Phi_{kl}(t')\, dt'} \, . \tag{30}$$

In the next section we apply the concepts and results presented above to the ferrofluid in the blocked limit.

VII. DYNAMICAL SUSCEPTIBILITY OF THE BLOCKED FERROFLUID

The starting point to apply the linear response approach of last section is the set of equations of motion for the system. We rewrite Eqs. (14) in the form of Eq. (15), by

defining the variables $v = \dot{\theta}$ and $w = \dot{\phi}$. To simplify the notation we also introduce $\bar{S} = S_0/I_1$, $\bar{\lambda} = \lambda/I_1$ and write Eqs. (14) in the form

$$\dot{\theta} = v \ , \tag{31a}$$
$$\dot{\phi} = w \ , \tag{31b}$$
$$\dot{v} = w^2 \sin\theta\cos\theta - \bar{S}\, w \sin\theta - \bar{\lambda}\, v - \bar{S}\,\gamma\, H_0 \sin\theta \ , \tag{31c}$$
$$\dot{w} = -2\, v\, w \cot\theta + \bar{S}\, v\, \csc\theta - \bar{\lambda}\, w \ . \tag{31d}$$

By comparison of Eqs. (31) with Eq. (17) we see that the components of the vector $\boldsymbol{P}^0(\boldsymbol{Q}^0)$ are just the RHS's of Eqs. (31). From Eq. (20) we obtain the matrix elements $K_{ij}(t),\ i,j = \theta,\ \phi,\ v,\ w$. The only non zero elements are

$$\begin{aligned}
K_{\theta v} &= 1 \ ,\\
K_{\phi w} &= 1 \ ,\\
K_{v\theta} &= w^2(1 - 2\sin^2\theta) - \bar{S}(\gamma\, H_0 + w)\cos\theta \ ,\\
K_{vv} &= -\bar{\lambda} \ ,\\
K_{vw} &= (2\, w\cos\theta - \bar{S})\sin\theta \ ,\\
K_{w\theta} &= (2\, v\, w - \bar{S}\, v\cos\theta)/\sin^2\theta \ ,\\
K_{wv} &= (-2\, w\cos\theta + \bar{S})/\sin\theta \ ,\\
K_{ww} &= -2\, v\cot\theta - \bar{\lambda} \ ,
\end{aligned}$$

where $\theta = \theta(t)$, $v = v(t)$ and $w = w(t)$ are the solutions of Eqs. (31). For any given set of initial values θ_0, v_0 and w_0 it corresponds a set of functions $K_{ij}(t)$ (independent of ϕ_0) and, from Eqs,(21) and (24) follows the corresponding $Y_i^j(t)$ and $M_{ij}(t)$.

We assume now that a time-dependent perturbing magnetic field is applied perpendicular to the z-axis, i.e., $\boldsymbol{H}(t) = (H_x(t), H_y(t), 0)$. The interaction energy of this field with the particles magnetic moment is

$$W = -\boldsymbol{\mu}\cdot\boldsymbol{H} = -S_0\,\gamma\, H_x\, \sin\theta\cos\phi - S_0\,\gamma\, H_y\, \sin\theta\sin\phi \ .$$

The terms to be added to Eqs. (31c) and (31d) are

$$\begin{aligned}
\frac{-1}{I_1}\frac{\partial W}{\partial\theta} &= \gamma\bar{S}\cos\theta(H_x\cos\phi + H_y\sin\phi) \ ,\\
\frac{-1}{I_1\sin^2\theta}\frac{\partial W}{\partial\phi} &= \frac{\gamma\bar{S}}{\sin\theta}(-H_x\sin\phi + H_y\cos\phi) \ .
\end{aligned}$$

By adding this terms to the RHS of Eqs. (31c) and (31d), respectively, comparing with Eqs. (15) and (16), and identifying F with H, we can write down the matrix $\widetilde{A}$:

$$\widetilde{A} = \begin{pmatrix} A_{\theta x} & A_{\theta y} \\ A_{\phi x} & A_{\phi y} \\ A_{vx} & A_{vy} \\ A_{wx} & A_{wy} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ \gamma\bar{S}\cos\theta\cos\phi & \gamma\bar{S}\cos\theta\sin\phi \\ -\gamma\bar{S}\sin\phi/\sin\theta & \gamma\bar{S}\cos\phi/\sin\theta \end{pmatrix} \tag{32}$$

To calculate the response functions $\Phi_{kl}(t)$ by Eq. (29) only the matrix elements at time zero are needed. For this purpose we substitute θ and ϕ in Eq. (32) by θ_0 and ϕ_0.

To complete the argument of the average in Eq. (29) we still need the $B_{k,i}(t)$. As the observable vector $\boldsymbol{B}$ we choose the projection of the magnetic moment $\boldsymbol{\mu}$ on the $\widehat{xy}$-plane, i.e., $\boldsymbol{B} = (B_x,\ B_y)$, with

$$\begin{aligned} B_x &= \gamma\, S_0 \sin\theta\, \cos\phi\ , \\ B_y &= \gamma\, S_0 \sin\theta\, \sin\phi\ . \end{aligned}$$

From Eq. (26) we then get

$$B_{x,\theta} = \gamma\, S_0 \cos\theta\, \cos\phi\ , \tag{33a}$$
$$B_{x,\phi} = -\gamma\, S_0 \sin\theta\, \sin\phi\ , \tag{33b}$$
$$B_{y,\theta} = \gamma\, S_0 \cos\theta\, \sin\phi\ , \tag{33c}$$
$$B_{y,\phi} = \gamma\, S_0 \sin\theta\, \cos\phi\ , \tag{33d}$$

and all other $B_{k,i}$ are zero.

For the response function $\Phi_{xx}(t)$ we obtain, from Eq. (29)

$$\Phi_{xx}(t) = \langle B_{x,\theta} M_{\theta v} A_{vx} + B_{x,\theta} M_{\theta w} A_{wx} + B_{x,\phi} M_{\phi v} A_{vx} + B_{x,\phi} M_{\phi w} A_{wx} \rangle_0\ , \tag{34}$$

with time arguments $B_{x,i}(t),\ M_{ij}(t,0)$ and $A_{jx}(0)$. Substituting the $B_{x,i}$ and A_{jx} by their values as given by Eqs. (33) and (32), writing $\phi(t) = \phi_0 + \Delta\phi$, where $\Delta\phi$ is independent of ϕ_0 (because the unperturbed equations do not contain ϕ) and using some trigonometric relations, the average over ϕ_0 in Eq. (34) may be done analytically, resulting in

$$\begin{aligned} \Phi_{xx}(t) = \Bigg\langle \frac{\gamma^2\, S_0 \bar{S}}{2} \Bigg[&\cos\theta\, \cos\theta_0 \cos\Delta\phi\ M_{\theta v} + \frac{\cos\theta}{\sin\theta_0} \sin\Delta\phi\ M_{\theta w} + \\ &- \sin\theta\, \cos\theta_0\, \sin\Delta\phi\ M_{\phi v} + \frac{\sin\theta}{\sin\theta_0} \cos\Delta\phi\ M_{\phi w} \Bigg] \Bigg\rangle_0\ . \end{aligned} \tag{35}$$

By the same procedure we obtain the other response functions:

$$\begin{aligned} \Phi_{xy}(t) = -\Phi_{yx}(t) = \Bigg\langle \frac{\gamma^2\, S_0 \bar{S}}{2} \Bigg[&\cos\theta\, \cos\theta_0 \cos\Delta\phi\ M_{\theta v} + \frac{\cos\theta}{\sin\theta_0} \sin\Delta\phi\ M_{\theta w} + \\ &- \sin\theta\, \cos\theta_0\, \sin\Delta\phi\ M_{\phi v} + \frac{\sin\theta}{\sin\theta_0} \cos\Delta\phi\ M_{\phi w} \Bigg] \Bigg\rangle_0\ . \end{aligned} \tag{36}$$

Eq. (36) also shows that Onsager's relation

$$\Phi_{yx}(t, -H_0) = \Phi_{xy}(t, H_0)\ ,$$

is satisfied, because Φ_{xy} is odd under $H_0 \to -H_0$. We also obtain $\Phi_{yy} = \Phi_{xx}$, which is an obvious result, from symmetry.

VIII. NUMERICAL RESULTS AND CONCLUSIONS

The equilibrium average indicated in Eqs. (35) and (36) are, in principle, to be done over θ_0, v_0, w_0 and all particle's independent parameters (polydispersity). The average over ϕ_0 was already performed analytically. However, the deviations of v and w from their most probable values are rapid fluctuations due to the Brownian noise, which is not present in our system of equations. Therefore, the choice of initial distribution, to be consistent with our approximation of neglecting the noise, should not include this fluctuations. We will use Boltzmann's equilibrium distribution for θ_0 and, for every selected value of θ_0, we chose v_0 and w_0 from an approximate solution of Eqs. (31c) and (31d) around $t = 0$, calculated in the following way:

1) Assume that if v is not zero at $t = 0$, when we disconnect the noise, it relaxes to zero according to the equation $\dot{v} = -\bar{\lambda}\, v$. Eq. (31c) then leads to

$$w_0 = \frac{\bar{S} - \sqrt{\bar{S}^2 + 4\gamma H_0 \bar{S}\cos\theta_0}}{2\cos\theta_0}\ , \tag{37}$$

where we have chosen the $-$ sign because w_0 has to vanish for $H_0 = 0$.

2) Analogously, we assume that if w is not w_0, it relaxes to w_0 according to the equation $\dot{w} = -\bar{\lambda}\,(w - w_0)$. Eq. (31d) then leads to

$$v_0 = \frac{\bar{\lambda}\, w_0}{\bar{S} - 2\, w_0\, cos\theta_0}\ . \tag{38}$$

This prescription was used in Sec.V for the initial velocities in the calculation which led to Figs. 1-b and 1-c. We remark that this choice of w_0 is meaningful only if

$$\bar{S} + 4\gamma H_0 \cos\theta_0 \geq 0\ . \tag{39}$$

However, if $\gamma\, S_0\, H_0/k_B T$ is not too small, the Boltzmann distribution becomes negligible for values of θ_0 such that Eq. (39) is not satisfied.

It is also important to examine under which circumstances the approximation made in Eq. (13), and in all that follows that equation, the neglecting of the noise terms, is appropriate. We are specially interested in obtaining the dynamical susceptibility of the system, and therefore we will examine the consequences of that approximation in the context of linear response. Two characteristic times are of importance: The longitudinal relaxation time $T_1 \approx \langle\dot{\theta}\rangle^{-1}$, where the average is over all magnetic particles, and the transverse relaxation time T_2, which is the time taken by the response functions to become approximately zero. We have borrowed the notation T_1 and T_2 from Magnetic Resonance (MR) because of the similarity of their meanings here and in NMR or EPR. The longitudinal (parallel to $\boldsymbol{H}_0$) relaxation, called "spin-lattice relaxation" in MR, occurs in a time T_1, via energy loss to the environment, due to the dissipative torque. The transverse relaxation, characterized by the vanishing of $\Phi_{xx}(t)$ and called "spin-spin relaxation" in MR, occurs in a time T_2, due to the loss of phase coherence between the responses of the different particles to a pulse of the

perturbing field at $t = 0$, in their rotations around $\boldsymbol{H}_0$. Since we assume that the system is very close to thermal equilibrium, at a given temperature, and since the longitudinal relaxation takes the system out of the initial equilibrium distribution corresponding to that temperature, just because the thermal noise is neglected in the equations of motion, our calculation of the response functions and susceptibility is only a good approximation if $T_2 \ll T_1$.

There are several sources of transverse relaxation. One of them is, of course, the noise, which is being neglected in this approximation. The different initial angles θ_0 and different particle's parameters I_1, λ, and S_0 (polydispersity) lead to different frequencies (see Eqs. (37) and (38)) and, consequently, to loss of phase coherence and to transverse relaxation. These are taken into account in the averaging procedure on Eqs. (35) and (36).

To obtain the functions $\theta(t)$, $\Delta\phi(t)$ and $M_{ij}(t)$ we have to solve the systems of differential equations, Eqs. (21) and (31). We have done it with the Runge-Kutta algorithm, in a workstation. The particle's parameters, field intensity and time unit have been arbitrarily chosen and kept the same in all calculations whose results are shown in the figures, except where explicitly stated.

Polydispersity was treated for particles made of the same material and having the same shape, assuming a uniform distribution of a linear dimension, r, in an interval of size Δr, i.e., r was chosen to be uniformly distributed in the interval $(1 - \frac{1}{2}\Delta r,\ 1 + \frac{1}{2}\Delta r)$. The other particle's parameters were scaled accordingly, namely,

$$\begin{aligned}
&S_0 \propto r^3, \quad I_1 \propto r^5, \\
&\bar{S} = S_0/I_1 \propto r^{-2}, \\
&\lambda \propto r^3, \quad \bar{\lambda} = \lambda/I_1 \propto r^{-2}.
\end{aligned}$$

The average over the initial angle θ_0 was weighted with the Boltzmann equilibrium distribution,

$$P(\theta_0) \propto \sin\theta_0 \, \exp(S_0 \, \gamma \, H_0 \, \cos\theta_0/k_B T) \ ,$$

and the temperature was chosen so that $S_0 \, \gamma \, H_0 \, \cos\theta_0/k_B T \approx 5$, so that $P(\theta_0)$ has a maximum around $\pi/6$.

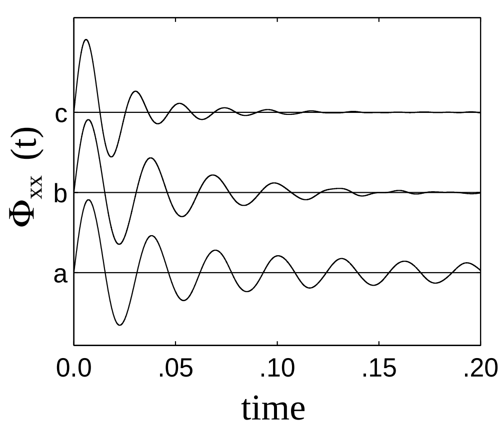

Fig.2: $\Phi_{xx}(t)$ versus time. Line a: $\Delta r = 0$; Line b: $\Delta r = 0.05$; Line c: $\Delta r = 0.20$.

Fig.2 shows the diagonal response function $\Phi_{xx}(t)$ versus time, for three different polydispersity ranges, $\Delta r = 0,\ 0.05$ and 0.20, for the curves a, b and c, respectively. This figure confirms what we said above that polydispersity causes the relaxation time T_2 to decrease. Their values, for the curves a, b and c, may be estimated to be approximately $T_2 \approx 0.2,\ 0.1$ and 0.05, respectively. The longitudinal relaxation time T_1 cannot be estimated from this curves, but has to be calculated together with the numerical solution of Eqs. (31), by using $T_1 \approx \langle\dot{\theta}\rangle^{-1}$.

The result is not strongly dependent on polydispersity, giving, in the present case, $T_1 \approx 20$. Therefore the condition stated above for the appropriateness of the approximation of neglecting the explicit presence of noise in the equations of motion, $T_2 \ll T_1$, is amply satisfied for the parameters used here.

Fig.3 and Fig.4 show the real and imaginary parts of the susceptibility $\chi(\omega)$, respectively, corresponding to the response functions of Fig.2. Among other information, Fig.4 shows clearly that the broader the dispersity of particle's size, the broader also the resonance line, as one should expect.

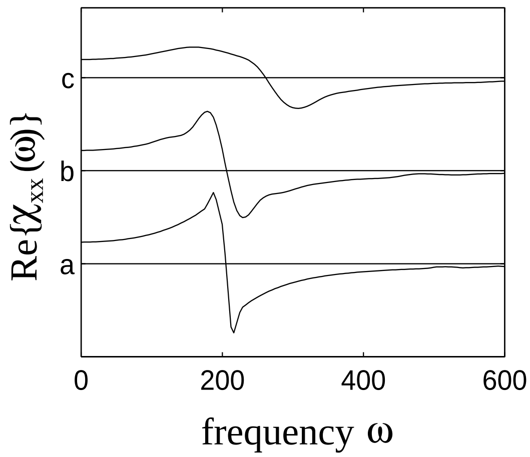

Fig.3: Real part of the susceptybility $\chi(\omega)$, versus ω, corresponding to the response functions of Fig.2.

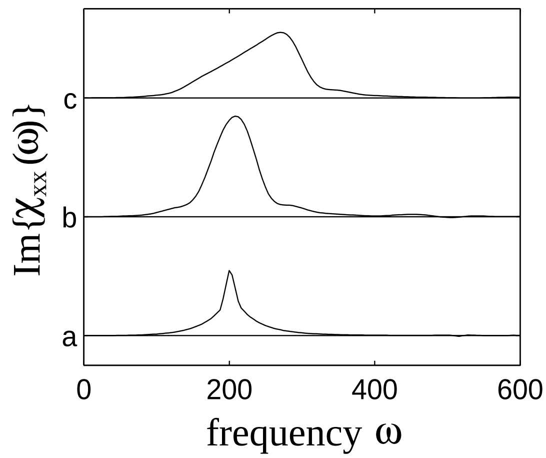

Fig.4: Imaginary part of the susceptybility $\chi(\omega)$, versus ω, corresponding to the response functions of Fig.2.

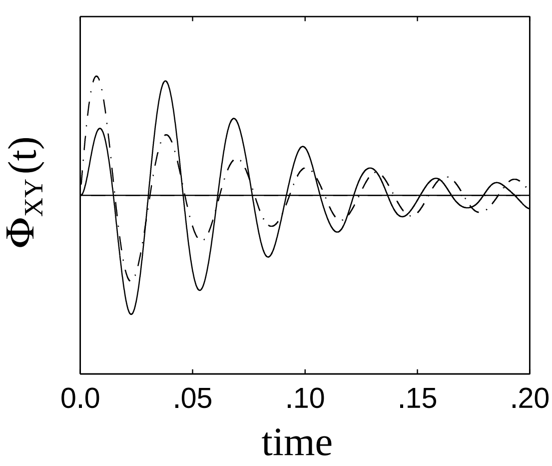

Fig.5: Solid line: $\Phi_{xy}(t)$; dot-dash line: $\Phi_{xx}(t)$, the same as in Fig.2-a.

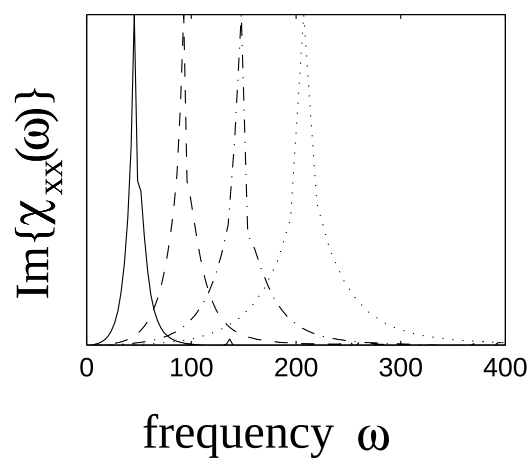

Fig.6: Imaginary part of the suceptibility for different values of the moment of inercia, I_1. Full line: $I_1 = 1.0$; dashed line: $I_1 = 0.25$; dot-dash line: $I_1 = 0.10$; dotted line: $I_1 = 0.05$.

Fig.5 shows the non diagonal response function $\Phi_{xy}(t)$ (solid line), for a monodisperse sample, plotted together with $\Phi_{xx}(t)$ (dot-dash line) for comparison. In Fig.6 we compare the resonance frequency (center of the resonance peak in the imaginary part of the susceptibility), for different values of the moment of inertia, I_1, keeping constant all other parameters. The lowest value, $I_1 = 0.05$ (dotted line) is the same as used in the previous figures, for monodisperse samples. The other curves correspond to $I_1 = 0.10$ (dot-dash line), 0.25 (dashed line) and 1.0 (full line). Clearly, the heavier the particles, the lower the resonance frequency.

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